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# Thermochemical and pore properties of goat-manure-derived biochars prepared from different pyrolysis temperatures

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ABSTRACT

In this work, goat manure (GM) was evaluated as a potential feedstock for preparing biochar. Its thermochemical characteristics were first investigated by the proximate analysis, calorific value, organic and mineral component analysis, showing that the biomass obviously comprises a large percentage of volatile matter and less amount of fixed carbon. A series of pyrolysis experiments were conducted to produce biochars (i.e., GMBC) from dry GM at different pyrolysis temperatures (673, 773, 873, 973, and 1073 K) held for 30 min. To evaluate their potential for soil amendment and energy use, the resulting biochars were subject to the analyses of chemical and physical properties, including proximate analysis, elemental analysis, calorific value, mineral components, true density, and surface area/pore volume. Based on the thermochemical properties, pyrolysis temperature at around 873 K seemed to be suitable for the production of GMBC, where its calorific value (CV) (i.e., 16.28 MJ/kg) only increased about 25% as compared to CV of the dry GM (i.e., 13.06 MJ/kg). However, the temperature of around 1073 K was found to be the pyrolysis conditions for producing porous carbon-like material with the maximal BET surface area (over 93 $m^2\ g^{-1}$) and porosity (about 0.115).



## 1. Introductio

With rising threats of the greenhouse effect and energy exhaustion, the world is facing energy-related threats concerning supply and environmental harm. Currently, solar and wind energy are the main candidates to replace fossil fuels; however, biomass energy (bioenergy) is another option with great potential to ensure clean energy production using thermochemical or biological conversion technologies. The driving force for using biomass resources is mainly due to renewability benefits, environmental benefits, and sociopolitical benefits [1]. As compared to fossil fuels, biomass is a renewable and locally abundant resource, thus providing economical carbon-neutral feedstock for energy production as well as mitigating global warming because of avoiding greenhouse gas (GHG) emissions. In this respect, non-woody biomass offers a large potential for energy use and other environment-friendly uses that are currently being utilized because it contains large amounts of lignocellulosic constituents [2].

In the livestock sector (LS), the main sources and types of GHG are carbon dioxide ($CO_2$) from land use and its changes (feed production, deforestation), nitrous oxide ($N_2O$) from manure and slurry management, and methane ($CH_4$) production from ruminants [3]. The LS is responsible for 18% ($CO_2$ equivalent) of total GHG emissions based on Food and Agriculture Organization (FAO) estimates, a share much larger than that emitted from transport sector [4]. The livestock animals that locally produce large quantities of excreta/manure are cattle, swine (hog and pig) and goat (sheep and lamb). Although livestock manures have relatively higher heating values on a dry basis, many farmers returned the collected manures to the soil as fertilizer. For example, the heating manure of goat manure is about 17.8 MJ/dry kg, higher that those (i.e., 17.0 and 13.5 MJ/dry kg, respectively) of swine manure and chicken manure [5]. According to the previous study [6], anaerobic digestion of manures has been performed on many plants for several decades and has been considered a technically proven and commercially attractive process for renewable energy production. However, these processes often faced with several problems including low energy yield, odorous nuisance, asphyxia poisoning, and infectious pathogen. In this respect, thermochemical conversion (TCC) of various biomass materials to produce biofuels or chemicals is gaining momentum [5].

A wide range of conversion technologies have been developed and thermochemical conversion (TCC) is gaining popularity for its high efficiency in terms of quality and product yield. TCC is a

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high-temperature chemical reforming process that breaks apart the bonds of organic matter and transforms the intermediates into char, synthesis gas, and a highly oxygenated bio-oil [7]. The most common TCC process is pyrolysis, which is generally described as the thermal decomposition of the organic components (long polysaccharides) in biomass in an inert atmosphere at mediate temperature to yield biochar (charcoal or biocoal). Consequently, this thermal process not only improves the thermochemical properties of biomass, but also produces a hydrophobic solid product with an increased mechanical property. Furthermore, it was successfully performed to convert swine manure into porous biochar pertinent to its potential use as a soil amendment [8,9]. During pyrolysis, process parameters (temperature, heating rate, holding time, and feedstock type) are the main factors governing the properties of biochar [10]. However, as reported by Downie et al. [11], pyrolysis temperature is the most important factor because thermochemical (TC) changes (e.g., the release of volatiles and condensable compounds from the unorganized phase of biomass) are all temperature dependent. In general, the pyrolysis process of using a slow heating rate ($\leq$20 K/min) and a long holding time ($\leq$60 min) is preferred to maximize the biochar production [1]. However, longer holding time will result in over-oxidization and formation of more char, but be not economical from the standpoint of process energy consumption.

Biochar is a charcoal-like and carbon-rich material with potential benefits in carbon sequestration [12], soil amendment [8,9,13], and climate change mitigation through reduction in GHG emissions when applied as soil amendment. In literature, many researches have revealed the TC properties of livestock and poultry manure-derived biochars as a sorbent for contaminant management in soil and water [14]. However, until recently, there is no literature on the utilization of goat manure (GM) in TCC processes. Therefore, the objective of this study was to evaluate the thermochemical and pore properties of goat-manure-derived biochars (GMBC) produced under different pyrolysis temperatures.

## 2. Materials and methods

### 2.1. Manure collection and preparation

Fresh GM was collected from the Environmental Center for Livestock Waste Management at National Pingtung University of Science and Technology (Pingtung, Taiwan). To avoid the environmental and health hazards, the manure sample was first dried by electronic oven at about 333 K for 72 h. After drying, the manure was crushed into smaller particles using a mortar and pestle. Prior to proximate analyses and pyrolysis experiments, the dry manure was stored in an oven chamber at 333 K to avoid moisture saturation. For the ultimate, elemental, and other fuel-related property analyses, the manure was further dried at 378 K, in terms of being on a dry basis.

### 2.2. Chemical analyses of dry goat manure

#### 2.2.1. Proximate analysis

The proximate analysis provides the weight percentages of moisture, volatile matter, fixed carbon and ash. Volatile matter (VM) was measured by difference in weight before and after furnace at 1223 K for 7 min. Similarly, ash content (AC) was determined by difference in weight before and after furnace at 1023 K for 4 h. According to the American Society for Testing and Materials (ASTM) Standard Test Methods (e.g., D-3172), moisture content (MC) was determined by heating manure samples in an oven at 378 K for 24 h and then calculated the difference in weight before and after heating. Finally, fixed carbon (FC) was calculated from the balance of the measured VM, AC, and MC (in wt%). The fixed carbon fuel ratio was determined as the ratio of fixed carbon to volatile matter (FC/VM). In order to evaluate the precision of measurement, it was carried out in triplicate.

#### 2.2.2. Calorific value

The calorific value (CV) of a biomass is indicative of its energy chemically bound in the biomass with reference to a standard condition. CV was measured in an adiabatic oxygen bomb calorimeter (Model No.: CALORIMETER ASSY 6200; Parr Co., USA). In the experiments, about 0.2 g of the oven-dried goat manure was conducted in the calorimeter to measure the constant volume heat released by the combustion of the biomass with pure oxygen. In this work, the measurement was also performed in triplicate.

#### 2.2.3. Ultimate analysis

The ultimate analysis determines the weight fractions of non-mineral major elements such as carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S). The composition of these elements is important in evaluating the thermochemical properties of manure. Using 2–3 mg of dry GM in three replications, these elements were analyzed using an elemental analyzer (Model No.: vario EL III; Elementar Co., Germany) with accuracy of 0.1% and precision of 0.2%. For each analysis, the standard samples (i.e., sulfanilic acid and benzoic acid) were first analyzed for checking the experimental error within $\pm$0.1%.

#### 2.2.4. Inorganic elemental analysis

An inductively coupled plasma-atomic emission spectrometer (Model No.: JY2000 2; Horiba Jobin Yvon, France) was used to determine the important nutrient and ash forming elements of dry GM (Ca, Cu, K, Mg, Mn, P, Zn, Si, Fe, and Al). Prior to the analysis, about 0.05 g of the manure sample was digested by a concentrated $HNO_3/H_2O_2$ solution in a pressure bomb to form a homogeneous solution. The digested solution was diluted with de-ionized water, and small amount of the diluted solution was used to measure its inorganic contents.

### 2.3. Pyrolysis experiments

The pyrolysis experiments at different temperatures held for 30 min were conducted and each was replicated twice. Using a vertically fixed-bed reactor [15], resulting biochars were produced from the dry GM under different temperature levels (673–1073 K). About 15 g of dry GM was put in a bottom-netted stainless-steel-holder and housed at the center of the tubular reactor. A sweep nitrogen gas ($N_2$) from a cylinder regulated (using a mass flow controller) at a constant flow rate of 500 cm$^3$/min was precisely metered into the pyrolysis system. The experimental condition in the pyrolysis system was performed at a fixed heating rate of about 10 K/min. The resulting biochar (after power-off for about 30 min of cooling) was taken out of the sample holder to weigh its mass and finally stored in an oven for subsequent characterization. The yields (or burn-off levels) were calculated by difference in mass before and after pyrolysis. The resulting biochars produced at 673, 773, 873, 973, and 1073 K (i.e., 400, 500, 600, 700, and 800 °C) for 30 min holding time were labeled as GMBC-400, GMBC-500, GMBC-600, GMBC-700, and GMBC-800, respectively.

### 2.4. Property analyses of biochar products

#### 2.4.1. Thermochemical characterization

The thermochemical property analyses (including proximate analysis, calorific value, ultimate analysis, and inorganic elemental analysis) in the biochar products were determined

according to the standard methods as previously described in the Section 2.2.

*2.4.2. True density*

True density (TD), also called helium-based solid density, is the ratio of sample mass to the intrinsic volume occupied by that mass. This physical property can be used to elucidate the thermal decomposition mechanism of biomass during the pyrolysis [15,16]. A helium displacement method with a pycnometer (Model No.: AccuPyc 1340; Micromeritics Co., USA) was used to measure the TD of different biochar samples. The device works by pumping helium gas into the sample chamber until the helium completely surrounds the sample. The expansion valve then opens allowing the pressure to equilibrate, after that, the device calculates the volume of the sample by comparing it with the empty reference chamber.

*2.4.3. Pore property*

The Brunauer–Emmett–Teller (BET) standard method, applied in a relative pressure ranging from 0.05 to 0.35, was used to obtain the BET surface area of different biochar samples in a surface area and porosity analyzer (Model No.: ASAP 2020; Micromeritics Co., USA). Total pore volume was calculated by converting the amount of nitrogen gas adsorbed at a relative pressure of 0.99 to the volume of liquid adsorbed. The estimation of pore diameter or average pore size was calculated by the measured values of surface area and total pore volume based on the assumption of a straight, cylindrical and un-interconnected pore shape [17]. From the data of total pore volume ($V_t$) and true density ($\rho_s$), the particle density ($\rho_p$) and porosity ($\varepsilon_p$) of biochar can be thus obtained as follows [17]:

$$\rho_p = \frac{1}{V_t + (1/\rho_s)}$$

$$\varepsilon_p = \frac{1}{\rho_p/\rho_s}$$

## 3. Results and discussion

*3.1. Thermochemical characterization of dry goat manure*

Table 1 summarized the thermochemical properties of dry goat-manure (GM). It is evident that the biomass comprises a large percentage of volatile matter (i.e., 69.5 wt%). The contents of moisture and fixed carbon (FC) in the sample are only 8.7 and 4.5 wt%, respectively. Furthermore, the ratio of fixed carbon (FC) to volatile matter (VM) refers to its fuel ratio. The fuel ratio of the dry GM (4.5 wt%/69.5 wt%) is 0.06 and is the main property that determines the rank of any biomass fuel. FC is the solid combustible residue that remains after a particular biomass is heated and the VM expelled. Thus, FC is used as an estimate of the amount of coke that will be yielded from a solid fuel [5]. However, this FC is less than the ultimate carbon content (Table 1) because some of the carbon is being removed in the form of hydrocarbons in the VM. Although high MC is a major characteristic of biomass, maintaining low feedstock MC will permit its rapid thermochemical conversion, which is related to the energy cost in processing the biomass. In this study, GM contains relatively lower MC (8.7 wt%) compared to 13.6 wt% for separated swine solids [9]. Further, the ash content in the GM is relatively higher than those contents in common biomass fuels such as sugarcane bagasse and switch grass, but slightly lower than rice-related residues such as rice husk and rice straw [18,19].

Regarding the fuel-related properties of biomass, its CV should be the most important one. As seen in Table 1, the CV of the dry GM was only about 13 MJ/kg on a dry basis, which was relatively lower than the data (i.e., 15–20 MJ kg$^{-1}$) on biomass residues and cattle manures [18,20]. According to the study by Jenkins et al. [19], each 1% increase in ash translates roughly into a decrease of 0.2 MJ/kg of CV. As described above, the biomass manure obviously comprised a high ash content, confirming that the carbon content of the dry GM was slightly lower than those of cattle manure (on average, 45.4%) [21,22], thus lessening its heating value.

The ultimate analysis in Table 1 revealed the high contents of carbon (C), hydrogen (H) and oxygen (O), indicating that the undigested forage contained in this livestock residue. In comparison with the molar ratios (i.e., 1.67/0.83 and 1.60/0.8, respectively) of H/C and O/C for cellulose and hemicellulose, respectively [5], the data on H/C and O/C for the dry GM are about 1.75 and 0.77, respectively. In this respect, the major organic compositions of the dry GM should be lignocellulosic constituents, which was consistent with its high VM value (i.e., 69.5 wt%). Although the nitrogen content (about 2.0 wt%) of the manure sample is lower than those of cattle manure (on average, 3.3% N) [21,22], but it is relatively high as compared to those (below 1 wt%) of most of energy crops and field crops [18]. As a result, the fuel-bound nitrogen will contribute to nitrogen oxides ($NO_x$) emissions from the combustion of the manure or its derived products (e.g., biochar). More significantly, the sulfur content in the dry GM was less than detectable limit by the elemental analyzer, meaning that sulfur oxides ($SO_x$, one of acidic pollutants) would not be emitted while combusting the manure or its derived biochar.

The ash-forming elements in the dry GM included Si, K, Ca, Mg, Al, Fe, S, and P (Table 1). It was shown that the dry GM contained high percentage of important nutrient elements (Ca, P, K, and Mg). The result was consistent with recent findings on mineral composition and ash content analyses for six major energy crops [23]. However, these alkali metals and alkaline earth metals could be present in the forms of oxides such as $K_2O$, $CaO$, $P_2O_5$ and $MgO$, which can lead to serious erosion, agglomeration, fouling, deposition, and corrosion in boiler or gasifier [24,25]. Table 1 also gave the contents of some heavy metals in the dry GM, indicating that ashes contained very low concentrations of manganese (Mn), copper (Cu) and zinc (Zn). By contrast, these toxic elements are of significant concern in the swine-based manure [26].

**Table 1**
Proximate analysis, ultimate analysis, and mineral composition of dry goat manure.

| Property | Value[a] |
|---|---|
| Proximate analysis (wt%)[b] | |
| Volatile matter | 69.5 ± 0.44 |
| Ash content | 17.3 ± 0.20 |
| Moisture content | 8.7 ± 0.08 |
| Fixed carbon[b] | 4.5 |
| Calorific value (MJ/kg)[c] | 13.06 ± 0.14 |
| Ultimate analysis (wt%)[c] | |
| Oxygen (O) | 41.16 ± 0.06 |
| Carbon (C) | 40.09 ± 0.04 |
| Hydrogen (H) | 5.85 ± 0.05 |
| Nitrogen (N) | 1.95 ± 0.04 |
| Sulfur (S) | ND[d] |
| Inorganic elements (wt%)[c] | |
| Calcium (Ca) | 3.52 ± 0.01 |
| Phosphorus (P) | 1.86 ± 0.01 |
| Potassium (K) | 1.64 ± 0.01 |
| Magnesium (Mg) | 1.29 ± 0.01 |
| Silicon (Si) | 1.15 ± 0.02 |
| Iron (Fe) | 0.21 ± 0.01 |
| Aluminum (Al) | 0.18 ± 0.004 |
| Zinc (Zn) | 0.06 ± 0.002 |
| Manganese (Mn) | 0.06 ± 0.001 |
| Cupper (Cu) | ND |

[a] Means with standard deviations for three replications.
[b] By difference.
[c] Dry basis.
[d] Not detected.

**Table 2**
Ultimate analysis and mineral composition of GMBC at different pyrolysis temperatures (673–1073 K) held for 30 min.

| Property | GMBC-400[a] | GMBC-500 | GMBC-600 | GMBC-700 | GMBC-800 |
|---|---|---|---|---|---|
| Yield (wt%) | 44.5 ± 0.29 [b] | 40.6 ± 0.01 | 37.9 ± 1.36 | 35.5 ± 2.01 | 33.8 ± 0.97 |
| Ultimate analysis (wt%)[c] | | | | | |
| Carbon (C) | 42.7 ± 0.04[d] | 42.3 ± 0.30 | 44.9 ± 0.08 | 42.6 ± 0.01 | 43.6 ± 0.11 |
| Oxygen (O) | 30.1 ± 0.03 | 23.4 ± 0.19 | 20.2 ± 0.02 | 22.2 ± 0.01 | 21.7 ± 0.06 |
| Nitrogen (N) | 2.1 ± 0.02 | 1.9 ± 0.03 | 1.2 ± 0.08 | 1.3 ± 0.01 | 1.1 ± 0.04 |
| Hydrogen (H) | 1.7 ± 0.13 | 1.5 ± 0.06 | 1.2 ± 0.04 | 0.9 ± 0.03 | 0.8 ± 0.09 |
| Sulfur (S) | ND[e] | ND | ND | ND | ND |
| Inorganic elements (wt%)[c] | | | | | |
| Calcium (Ca) | 6.7 ± 0.01 | 7.9 ± 0.02 | 9.4 ± 0.04 | 8.3 ± 0.03 | 9.3 ± 0.03 |
| Phosphorus (P) | 3.8 ± 0.12 | 4.4 ± 0.04 | 5.3 ± 0.04 | 4.8 ± 0.03 | 5.0 ± 0.09 |
| Potassium (K) | 2.9 ± 0.02 | 3.3 ± 0.05 | 3.4 ± 0.03 | 3.2 ± 0.03 | 3.3 ± 0.05 |
| Magnesium (Mg) | 2.4 ± 0.01 | 2.9 ± 0.01 | 3.2 ± 0.01 | 3.0 ± 0.01 | 3.3 ± 0.01 |
| Silicon (Si) | 2.3 ± 0.05 | 2.8 ± 0.11 | 3.0 ± 0.03 | 2.7 ± 0.08 | 3.1 ± 0.09 |
| Iron (Fe) | 1.8 ± 0.02 | 0.5 ± 0.01 | 0.6 ± 0.00 | 0.6 ± 0.00 | 1.3 ± 0.01 |
| Aluminum (Al) | 0.3 ± 0.00 | 0.4 ± 0.00 | 0.4 ± 0.00 | 0.4 ± 0.00 | 0.5 ± 0.00 |
| Zinc (Zn) | 0.2 ± 0.00 | 0.1 ± 0.00 | 0.3 ± 0.00 | 0.2 ± 0.00 | 0.1 ± 0.00 |
| Manganese (Mn) | 0.2 ± 0.00 | 0.1 ± 0.00 | 0.2 ± 0.00 | 0.2 ± 0.00 | 0.2 ± 0.00 |
| Cupper (Cu) | ND | ND | ND | ND | ND |

[a] GMBC produced at 400 °C (400 + 273 = 673 K), etc.
[b] Means with standard deviations for two experiments.
[c] Dry basis.
[d] Means with standard deviations for three replications.
[e] Not detected.

### 3.2. Yields of biochar products

Changes in the yields of goat-manure-derived biochars (GMBC) produced at different pyrolysis temperatures held for 30 min were shown in Table 2. Obviously, yields decreased significantly as temperature progressed. This trend should be attributed to the volatilization of tar products derived from the lignocellulosic components of the dry GM at high pyrolysis temperature. The greatest decrease in yield was observed at pyrolysis temperature of ranging from 673 K (400 °C) to 873 K (600 °C). Beyond 873 K, yield difference was reduced gradually because the decomposition of hemicelluloses and cellulose approaches near complete at higher temperatures [27]. It is therefore expected that beyond 1073 K, yield difference will become insignificant or even level off. This result was in close agreement with the findings by Ro et al. [28], who reported the yields of poultry litter and swine solid BC (pyrolyzed at 903 K) ranging from 43 to 49%. Results therefore suggest that pyrolysis temperature of around 873 K is sufficient for optimum GMBC yield.

### 3.3. Thermochemical properties of biochar products

#### 3.3.1. Proximate analysis

The effects of pyrolysis temperature on VM, AC, MC, and FC of biochar products (GMDB) were shown in Fig. 1. VM decreased with temperature while AC, MC, and FC were increased. The FC content was elevated from 4.5% in the dry GM to about 37% in GMBC-600 (873 K). The FC content of GMBC products increased with temperature and a maximal increase was recorded at 873 K. (Fig. 1). According to the study by Lee et al. [27], as pyrolysis progresses, H and O deplete in the BC and therefore become carbon-rich. From the environmental viewpoint, the FC content of BC showed its effectiveness in C sequestration because it represents the solid carbon in the biomass that remains in the char after devolatilization during the pyrolysis process [1]. Therefore, the higher the FC content, higher will be its effectiveness in climate change mitigation. Based on the data in Fig. 1, pyrolysis temperature at around 873 K seemed to be optimal for the production of GMBC.

#### 3.3.2. Elemental composition

Table 2 summarized the ultimate analysis and ash-forming inorganic elements of GMBC with pyrolysis temperature. The elemental composition of BC is important because the TC properties of solid fuels are relevant to it. The contents of organic elements in the BC products were influenced by pyrolysis temperature. For example, the carbon (C) content was increased from 42.7% (GMBC-400) to 44.9% (GMBC-600). On the other hand, oxygen (O), nitrogen (N), and hydrogen (H) contents showed a decreasing trend with temperature; and sulfur (S) and cupper (Cu) were not detected, which were consistent with the data in Table 1. In comparison with the findings by Song and Guo [29], the overall loss of N from poultry litter during pyrolysis was greater at higher pyrolysis temperature. The authors further stated that, as pyrolysis temperature exceeded 673 K, the majority of N was lost as volatiles (e.g., $N_2O$, NO, $NO_2$, and low molecular weight organic N). Furthermore, with increasing temperature, GMBC contained higher percentage of major and minor nutrient elements (Ca, P, K, Mg, Si, and Fe) and trace amounts of heavy metals (Al, Zn, Mn, and Cu) as compared to the data in Table 1. With regards to these inorganic elements, the problems of ash deposition at high pyrolysis temperatures is associated with first, the reaction of alkali with silica to form alkali silicates that melt or soften at low temperatures; and second, the reaction of alkali with sulfur to form alkali sulfates [19]. Therefore, the undetected levels of S in the dry GM and GMBC products will be of particular importance by avoiding reactions with alkali to form sulfates.

#### 3.3.3. Calorific value and fuel ratio

Regarding the fuel-related properties of biochar, its heating value should be the most important parameter. In Fig. 2, it can be seen that the calorific values (CV) of GMBC ranged from 15.8 to 16.4 MJ/kg on a dry basis, which were relatively lower than that (i.e., 28.0–32.0 MJ/kg) of fossil coal [5]. As compared to CV of the dry GM (i.e., 13.06 MJ/kg, seen in Table 1.), the calorific value of the biochar product (i.e., 16.28 MJ/kg for GMBC-600) only increased about 25%. Also seen in Fig. 2, CV increased with temperature but decreased beyond 873 K. Cantrell et al. reported similar decrease in CV as temperature was increased from 623 to 973 K [8]. The highest CV (16.3 MJ/kg) was recorded at 873 K (GMBC-600), a value higher than the CV of swine solids (15.07 MJ/kg) and poultry litter (14.75 MJ/kg) BC produced at 973 K [8]. The maximal increase in CV at 873 K is in close agreement with its elemental composition (Table 2). For example, the carbon content of GMBC-600 was 44.9%, larger than that of other GMBC. On the other hand, fuel ratio (FR), defined as the ratio of FC to VM, is also an important property

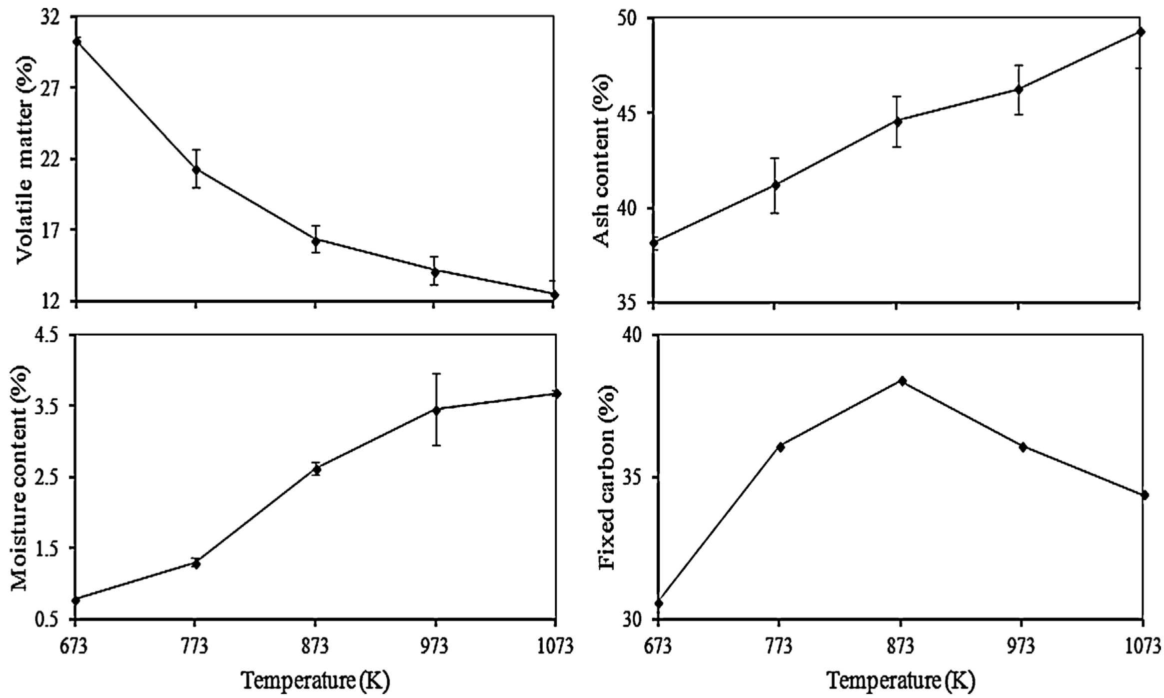


**Fig. 1.** Volatile matter, ash content, moisture content, and fixed carbon of GMBC with pyrolysis temperature.

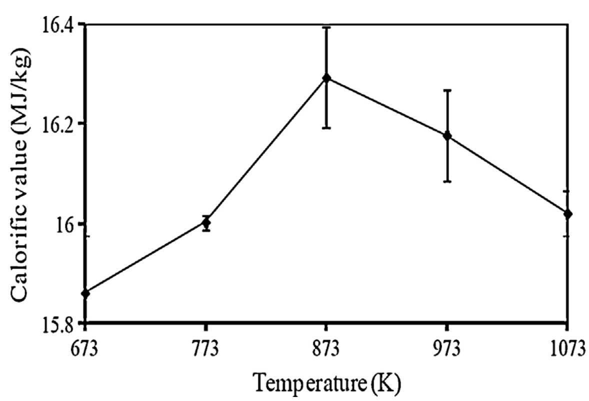


**Fig. 2.** Calorific values of GMBC with pyrolysis temperature.

in characterizing biofuels. FR was significantly increased from 0.06 (dry GM) to 2.73 (GMBC-600) as a function of pyrolysis temperature. In Fig. 3, there is a sharp increase in FR from 673 K to 873 K; and beyond 873 K, there was no significant increase. Therefore, for

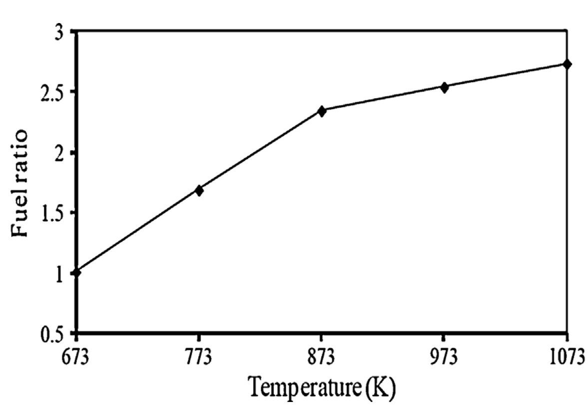


**Fig. 3.** Fixed carbon fuel ratios (FC/VM) of GMBC with pyrolysis temperature.

maximal increase in CV and FR, pyrolysis temperature of 873 K may be suitable for producing GMBC.

### *3.4. True density and pore properties of biochar products*

#### *3.4.1. True density*

The true density (TD, or $\rho_s$) of BC is relevant to its mechanical strength because of the increased order of molecules that favor a higher mechanical strength than the original feedstock. The significant loss of volatiles and condensable compounds from the unorganized phase of the pyrolytic biomass leads to an increase in TD. Hence, the TD of GMBC increased with temperature with a maximal increase at 873 K (Table 3). This increase could be attributed to active pyrolysis of cellulosic fragments and shrinkage processes, which result in an increased content of aromatic carbon clusters at higher temperatures forming a highly carbonaceous material with corrugated structure. In this respect, the TD of GMBC is an appropriate indicator of the extent of its carbonization, and it is in accordance with the pore properties, which will be described below.

#### *3.4.2. Pore properties*

The effects of pyrolysis temperature on the pore properties of GMBC were shown in Table 3. Based on the data in Table 3, the BET surface area of the dry GM is 0.05 $m^2 g^{-1}$; after pyrolysis, there was a significant increase with temperature. In the pyrolysis temperature range studied (i.e., 673–1073 K), the pore properties (e.g. BET surface area) of the resulting biochars increased with increasing temperature; i.e. GMBC-400 (3.3 $m^2 g^{-1}$) ≒ GMBC-500 (1.7 $m^2 g^{-1}$) < GMBC-600 (13.9 $m^2 g^{-1}$) < GMBC-700 (39.1 $m^2 g^{-1}$) ≒ GMBC-800 (93.5 $m^2 g^{-1}$). The findings were in close agreement with the previous study regarding the pyrolysis of separated swine manure [9]. More consistently, the morphological micrographs of the virgin sample (i.e., GM) and the resulting biochar (i.e., GMBC-800) with the magnification of 600–700 times were preliminarily illustrated in Fig. 4, showing the pore development between the surface textures of these samples. On the other hand, $N_2$

**Table 3**
Pore properties and true density of GMBC prepared from different pyrolysis temperatures (673–1073 K) held for 30 min.

| Property | GMBC-400 | GMBC-500 | GMBC-600 | GMBC-700 | GMBC-800 |
|---|---|---|---|---|---|
| BET surface area ($m^2 g^{-1}$) | 3.27 ± 0.25 | 1.68 ± 0.11 | 13.92 ± 0.84 | 39.08 ± 2.03 | 93.49 ± 5.11 |
| Total pore volume ($cm^3$/g) | 0.0013 | 0.0013 | 0.0078 | 0.0199 | 0.049 |
| Pore diameter (Å)[a] | 15.9 | 30.95 | 22.41 | 20.37 | 20.96 |
| Porosity[b] | 0.0026 | 0.0028 | 0.0187 | 0.0479 | 0.1145 |
| True density (g/$cm^3$)[c] | 1.98 ± 0.03 | 2.12 ± 0.03 | 2.44 ± 0.03 | 2.53 ± 0.04 | 2.64 ± 0.03 |
| Particle density (g/$cm^3$)[d] | 1.97 | 2.13 | 2.39 | 2.41 | 2.34 |

[a] Calculated from BET surface area and total pore volume.
[b] Calculated from the particle density and true density [17].
[c] Measured by the helium-displacement method.
[d] Calculated from the total pore volume and true density [17].

(a) GM

(b) GMBC-800

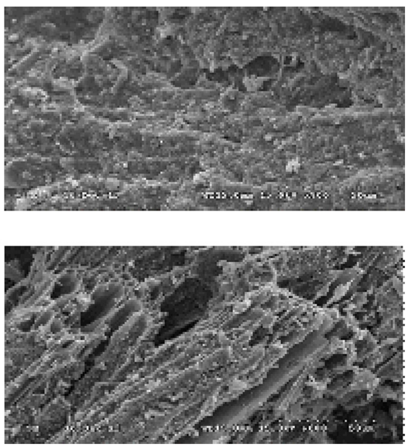

**Fig. 4.** Morphological micrographs of (a) goat manure (GM) and (b) GM-based biochar (i.e., GMBC-800) with the magnification of 600–700 times.

adsorption–desorption isotherms (Fig. 5) at 77 K of some goat-manure-biochars (i.e., GMBC-700 and GMBC-800) showed the presence of desorption hysteresis. The shapes of the isotherms in all samples were similar. It is clear that these isotherms are type IV which should be characteristic of the mesoporous materials due to the nitrogen condensation [30]. However, the values were observed to increase significantly above 973 K, which was possibly attributed to the rigorous reaction, resulting in that more pores are created in the resulting biochars (i.e., GMBC-700 and GMBC-800). In the study by Zhang et al. [31], high temperature causes micropores to widen as it destroys the walls between adjacent pores, resulting in the enlargement of pores and an increase in total pore volume. However, it should be noted that beyond 1073 K,

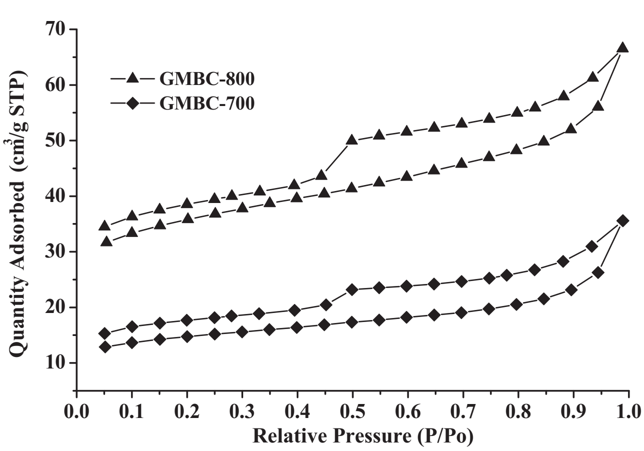


**Fig. 5.** $N_2$ adsorption–desorption isotherms of GM-based biochar products (i.e., GMBC-700 and GMBC-800).

there will be less increase in BET surface area due to structural ordering, pore widening, and/or the coalescence of neighboring pores, leading to a decrease in pore volume at post-softening and swelling temperatures [32]. In a similar study reported by Meng et al. [33], the BET surface area and pore volume of resulting biochars greatly depend on pyrolysis temperature. According to the authors, BET surface area generally increases with increasing temperature until it reaches the temperature at which deformation occurs, resulting in subsequent decreases in the pore properties.

## 4. Conclusions

In this work, the pyrolytic process was used to prepare a series of biochars (i.e., GMBC) from dried goat manure at temperature range from 673 to 1073 K. Based on the thermochemical properties, pyrolysis temperature at around 873 K seemed to be suitable for the production of GMBC, where the calorific value (CV) of the biochar product (i.e., 16.28 MJ/kg for GMBC-600) only increased about 25% as compared to CV of the dry GM (i.e., 13.06 MJ/kg). However, the temperature of around 1073 K was found to be the pyrolysis conditions for producing porous carbon-like material with BET surface area (over 93 $m^2 g^{-1}$) and porosity (about 0.115). Furthermore, the presence of nutrients (i.e., N, P, Ca, Mg, and K) rich in the resulting biochars could be pertinent to soil fertility. Although GMBC may be a potential alternative to fossil fuels, it is preferably used as a soil amendment and environmental remediation media due to its porous structure and high mineral-ash content.

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